AD-A191 262 TWO DIMENSIONAL COMPRESSIBILITY OF ELECTROCHEMICALLY ADSORBED LEAD ON SILVER (111)(U) PUERTO RICO UNIV RIO PIEDRAS DEPT OF PHYSICS O R MELROY ET AL. 28 JAN 88 1/1

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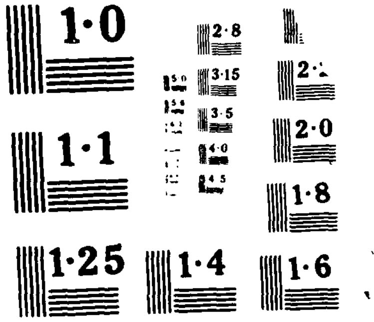
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TECHNICAL REPORT # 32

Two Dimensional Compressibility of Electrochemically Adsorbed Lead on Silver (111)

by

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Abstract

We report the two dimensional compressibility of electrochemically deposited lead on silver (111). Measurements were made in-situ (in contact with solution) using grazing incidence x-ray scattering. Between monolayer formation and bulk deposition, the near neighbor distance of the lead monolayer decreases linearly with applied potential, (proportional to the chemical potential). Since the lead monolayer is in equilibrium with the the lead in solution, the isothermal compressibility of the monolayer can be calculated and is 0.98 $\mathring{A}^2/eV$. Implications of the highly strained monolayer on the wetting behavior of lead are discussed.

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Adsorbed monolayers are of fundamental interest, since they provide physical realizations of two dimensional (2D) condensed matter. Considerable effort has been devoted to studying monolayers of gases physically adsorbed from the vapor phase onto graphite and metal substrates.[1-10] The isothermal compressibility (κ_2) of rare gas monolayers has been measured and agrees well with that calculated theoretically using relatively simple molecular interactions.[3-6] However, the compressibility of metallic adlayers has received far less attention due to inherent difficulties in making equilibrium adsorption measurements. Realistic calculations of κ_2 for metals are also considerably more difficult, since two dimensional band structure calculations that include the effect of the substrate are necessary. In this paper, we report an ***in-situ*** grazing incidence x-ray scattering (GIXS) investigation of electrochemically adsorbed lead on silver (111). Both the room temperature compressibility of the monolayer with applied potential and the wetting behavior have been studied.

Electrochemical deposition of metals onto a foreign metal substrate frequently occurs in distinct stages.[11] The initial steps, corresponding to the formation of different ad-layers on the electrode surface, occur at electrode potentials positive of the reversible thermodynamic potential for bulk deposition and hence are termed underpotential deposition (UPD). On single crystals, the different peaks in the current/potential profile prior to bulk deposition correspond to the formation of well defined, presumably ordered, ad-layers.[12-16] The current response to a linear sweep of potential for lead on silver (111) is shown in figure 1. The inset shows the integral of this or the adsorption isotherm. The first peak at approximately -350mV corresponds to the deposition of a single monolayer of lead. That this is an incommensurate, close-packed triangular monolayer has been inferred using a variety of techniques[12-14,17] and has recently been proved in an ***in-situ*** x-ray diffraction experiment.[18] Between the peak in the current at -350 mV and the onset of bulk deposition (-550mV), a single monolayer of lead, in

equilibrium with the lead ions in solution, is adsorbed on the silver surface. Varying the potential in this region between monolayer formation and bulk deposition changes the chemical potential and is thus analogous to varying the vapor pressure of a gas in equilibrium with its physisorbed monolayer.

The presence of the condensed phase (electrolyte) over the electrode, of course, greatly complicates measurements of UPD monolayers. Most techniques that give direct surface structural information are based on scattering of ions or electrons and are unsuitable for use outside high vacuum. Ex-situ surface science techniques have been used to study the structure of layers adsorbed from solution and have provided valuable information. However, these methods require transfer of the sample from the electrochemical environment, which introduces questions about surface rearrangement upon removal of the electrolyte and loss of potential control. GIXS is, however, ideally suited for ***in-situ*** structural measurements of the solid-liquid interface.

GIXS is a well established technique and has been applied to the structural determination of surface reconstruction on metals[19] and semiconductors,[20] the melting of adsorbed monolayers,[21] and the characterization of solid/solid interfaces.[22] To use GIXS to study UPD monolayers, a suitable electrochemical cell was developed that allows deposition with a thick layer of electrolyte covering the electrode.:SUP/18/ The cell is then reconfigured such that a very thin electrolyte layer covers the electrode. The thinness of this layer greatly reduces scattering from the electrolyte.

The electrode preparation and electrochemical cell have previously been described in detail and will not be discussed here.[18] Lead was electrochemically deposited at room temperature on the

silver (111) electrode at -400mV (vs Ag/AgCl) from a 0.1M sodium acetate, 0.1M acetic acid and 5×10^{-3} M lead acetate solution. The cell was the changed into the thin later configuration and experiments at different potentials conducted by varying the potential after the reconfiguration. The x-ray diffraction data were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) under dedicated beam conditions on a focussed 54-pole wiggler beam line (VI-2) equipped with a Huber four circle diffractometer on which the electrochemical cell was mounted. The sample was held in the vertical plane and the scattered radiation collected at an exit angel equal to the (grazing) incidence angle. The incident x-ray beam energy was chosen to be 12350 eV (1.003 Å) using a silicon (220) double crystal monochromator and calibrated with the diffraction from a silicon (111) crystal.

At potentials where lead is adsorbed (negative of -375mV), diffraction from the lead monolayer is observed. Radial and azimuthal scans of the (10) reflection of the lead monolayer with the electrode held at -550mV are shown in figure 2. The diffuse background scattering is largely due to the thin layer of solution covering the electrode. The peak in the radial scan appears at $Q = 2.13$ Å^{-1} corresponding to a lead-lead near neighbor distance of 3.40 Å for the incommensurate close packed monolayer. The lead monolayer is not aligned along a silver symmetry direction, but is rotated 4.5° from the silver $(\bar{2}11)$ direction.

As the potential of the electrode decreases from -375 to -550 mV, the scattering vector of the lead reflection increases. A plot of the lead-lead near neighbor distance vs. electrode potential is shown in figure 3. The near neighbor distance decreases linearly with potential until the onset of bulk deposition. At this potential, the near neighbor distance is 3.40Å, a 2.8% contraction from bulk lead. No additional change in the spacing is observed with potential beyond the the onset of bulk lead deposition. It should be recognized that the thin layer of

electrolyte covering the electrode only contains a few equivalent monolayers of lead so insufficient bulk lead is deposited to affect the first ad-layer.

The two dimensional (2D) isothermal compressibility κ_2 is defined as:[2]

$$\kappa_2 = -\left(\frac{1}{a}\right)\left(\frac{\partial a}{\partial \phi}\right)_T = -\left(\frac{\partial a}{\partial \mu}\right)_T \tag{1}$$

where ϕ is the 2D spreading pressure, a is the atomic area, and μ is the chemical potential. For a physisorbed monolayer in equilibrium with its (ideal gas) vapor,[2] $d\mu = -k_B T\,(d\ln P)_T$. This equilibrium relationship has been used in previous experimental measurements of κ_2.[3-6] Similar experiments on metallic ad-layers have not been possible because the very low vapor pressure of the metals necessitates the use of nonequilibrium conditions. However, changing the applied potential in electrochemical adsorption experiments is analogous to changing the vapor pressure in the gas adsorption experiments, since the chemical potential is related to the applied potential (V) as:[23]

$$d\mu = -\,z\,e\,dV \tag{2}$$

where z is the number of electrons transferred per atom deposited and e is the electron charge. Thus κ_2 can be determined from equilibrium measurements of either pressure or applied potential. However, in electrochemical experiments the potential can be accurately controlled over a wide range without the experimental difficulties of controlling and measuring pressure over a large range ($d\mu \propto d\ln P$).

For a close-packed triangular layer, $a = \frac{\sqrt{3}}{2} r^2$, and

$$\kappa_2 = \frac{\sqrt{3}\, r}{ze} \left(\frac{\partial r}{\partial V} \right)_T \qquad (3)$$

Evaluating the slope from figure 3 and substituting above, the value obtained for κ_2 is 0.98 $Å^2$/eV. This is in reasonable agreement with that (1.2 $Å^2$/eV) estimated for a 2D Sommerfeld model (non-interacting free electron gas),[24] which is probably a result of the free-electron nature of lead. A more realistic calculation would involve a 2D band structure calculation that included effects of the silver substrate and is outside the scope of this letter. Since the slope in Figure 3 is constant, κ_2 is independent of near-neighbor spacing, to within 3%. This is unexpected, since in bulk lead the compressibility drops by 7% when the near neighbor distance decreases from 3.45 to 3.40 Å.[25]

As shown in Figure 2, the angle between the lead (10) reflection and the silver $(\bar{2}11)$ direction (rotational epitaxy angle) is 4.5°. Surprisingly, no change in this angle was observed with the compression of the ad-layer. The application of the models developed either by Novaco and McTague[7] (weakly modulated overlayer) or Shiba[8] (large modulations in adatom-substrate energy) predict 0.5° or more changes in the rotation epitaxy angle over this compression. We were unable to detect any satellite diffraction that would result from a strong periodic modulation of the ad-layer by the substrate. However, the presence of diffuse scattering from the electrolyte prevents the observation of a satellite with less than 3% of the intensity of the (10) peak.

As shown above, at the potential for bulk deposition, the ad-layer is highly strained. Recent theories on wetting[26-28] have suggested that, in addition to the ratio between substrate-adsorbate and adsorbate-adsorbate interactions, strain in the adsorbed layers is an

important factor in determining wetting behavior. This strain is compression resulting from a strong adsorbate-substrate interaction. Although these theories were developed for physisorption and the detailed calculations are not applicable in our case, the idea that strain is a determining factor is relevant. At potentials where bulk lead was deposited, no change in the intensity of the adsorbate diffraction was observed. Clearly, a second layer of lead, in registry with the first, is not formed. In addition, no new diffraction spots were observed from bulk lead indicating that bulk lead is initially deposited as randomly oriented three dimensional islands (incomplete wetting). Although these findings are in agreement with the theories outlined above, care must be taken in drawing analogies between vacuum and electrochemical deposition. Solvent and electrolyte adsorption are often important in determining the structure of electrochemically deposited layers. Electrochemical deposition, however, has the advantage of allowing an equilibrium measurements. Just as this allows the two dimensional compressibility of metals to be measured, studies of electrochemical deposition may lead to significant insight into wetting behavior.

In summary, the variation in the lead near neighbor distance with applied potential was measured and the 2D isothermal compressibility determined for electrochemically adsorbed lead monolayers on silver (111). This equilibrium measurement is possible for metals because the chemical potential can easily be varied and the in-plane near neighbor distance measured in-situ using GIXS. In-situ structural studies of the solid-liquid interface are now possible using techniques such as GIXS and will lead to a greater understanding of nucleation at this interface The ability to make equilibrium measurements at this interface should also enhance our understanding of 2D layers.

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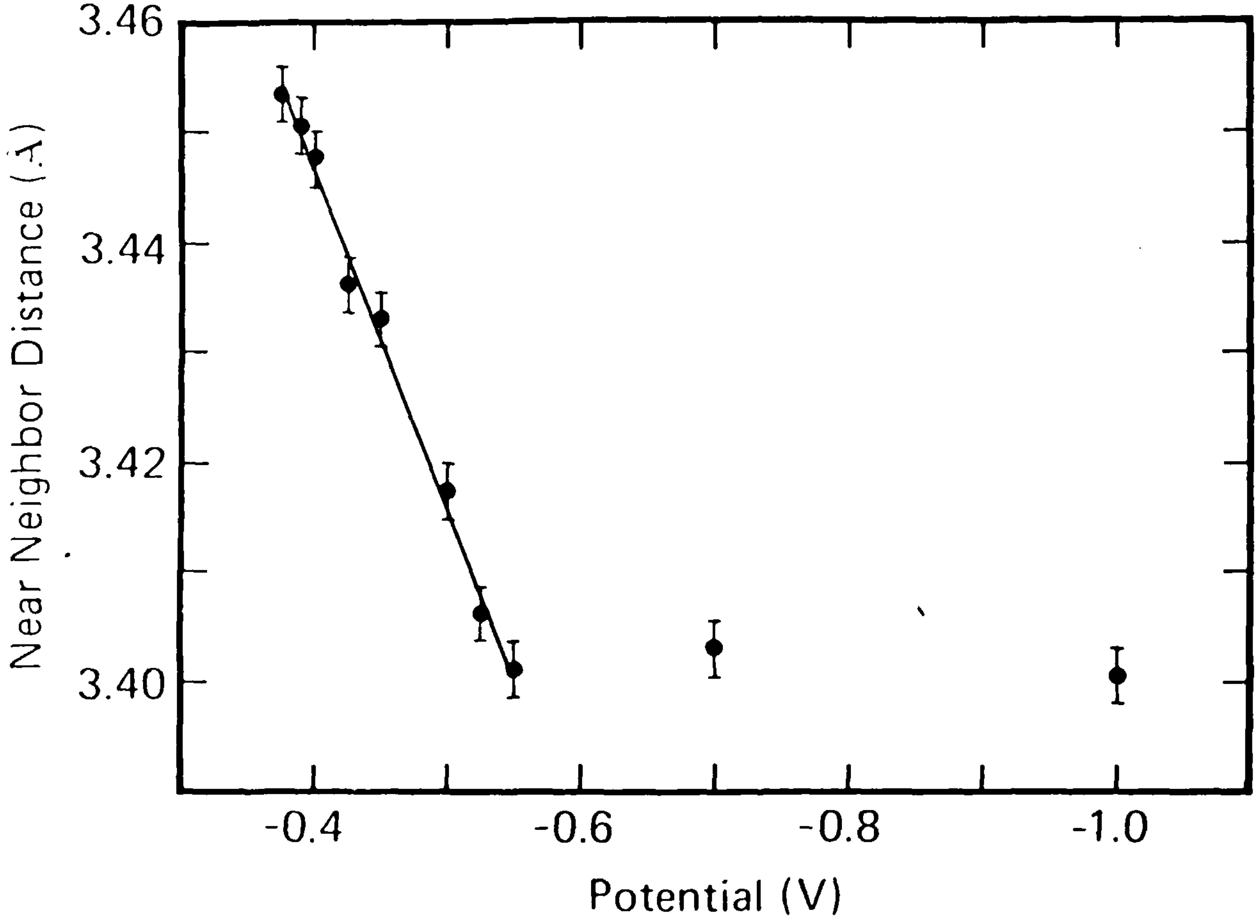
Figure Captions

Figure 1. Voltamogram for the deposition of lead on silver(111). Inset: Adsorption isotherm.

Figure 2. The (10) reflection of the lead monolayer on silver (111) at -550mV. The silver $(\bar{2}11)$ is defined as $\varphi = 0$. a) Rocking scan at $Q = 2.13\ \text{Å}^{-1}$. b) Radial scan at $\varphi = 4.5°$. The 0.02Å^{-1} width of the peak indicates a domain size of about 290 Å.

Figure 3. Lead-lead near neighbor distance vs electrode potential. The UPD monolayer adsorbs at -375mV and bulk lead is deposited at -550mV.



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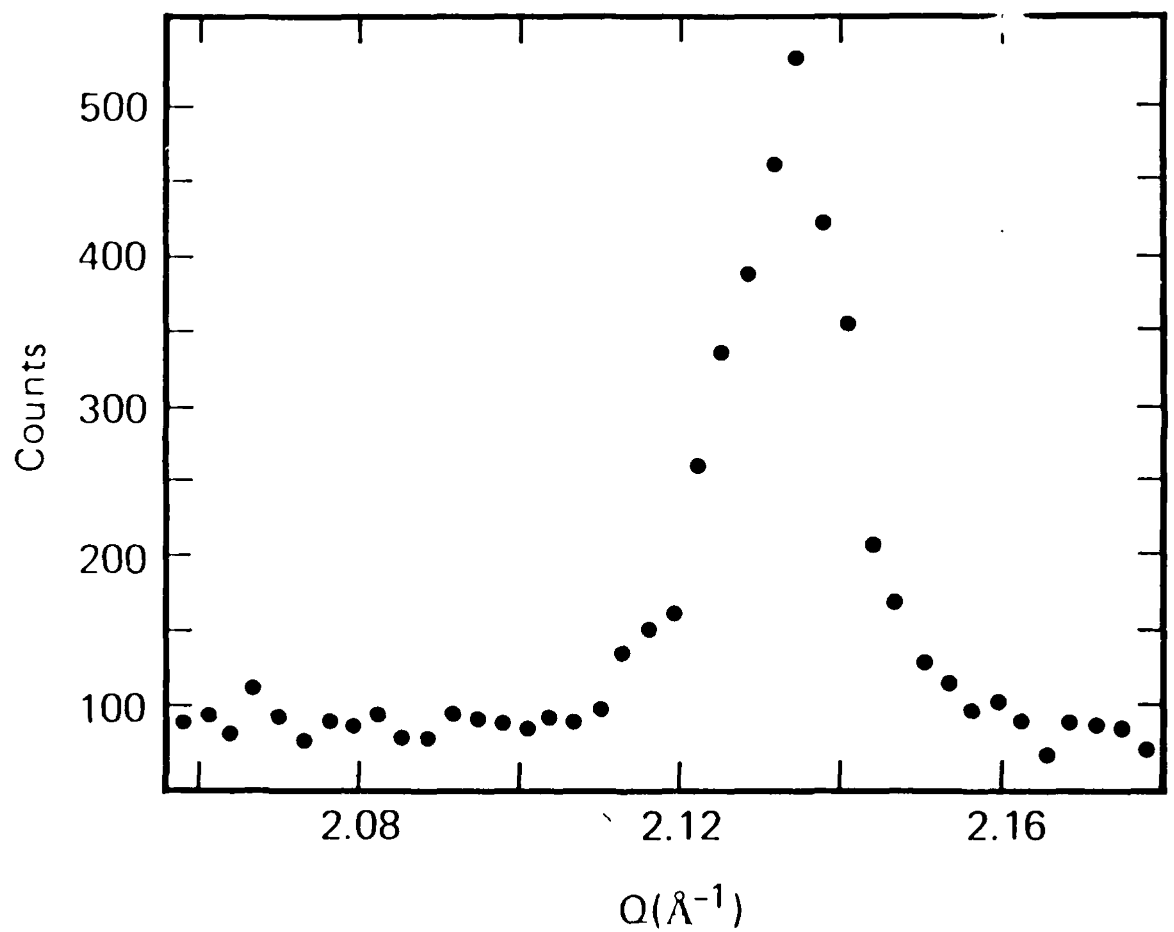
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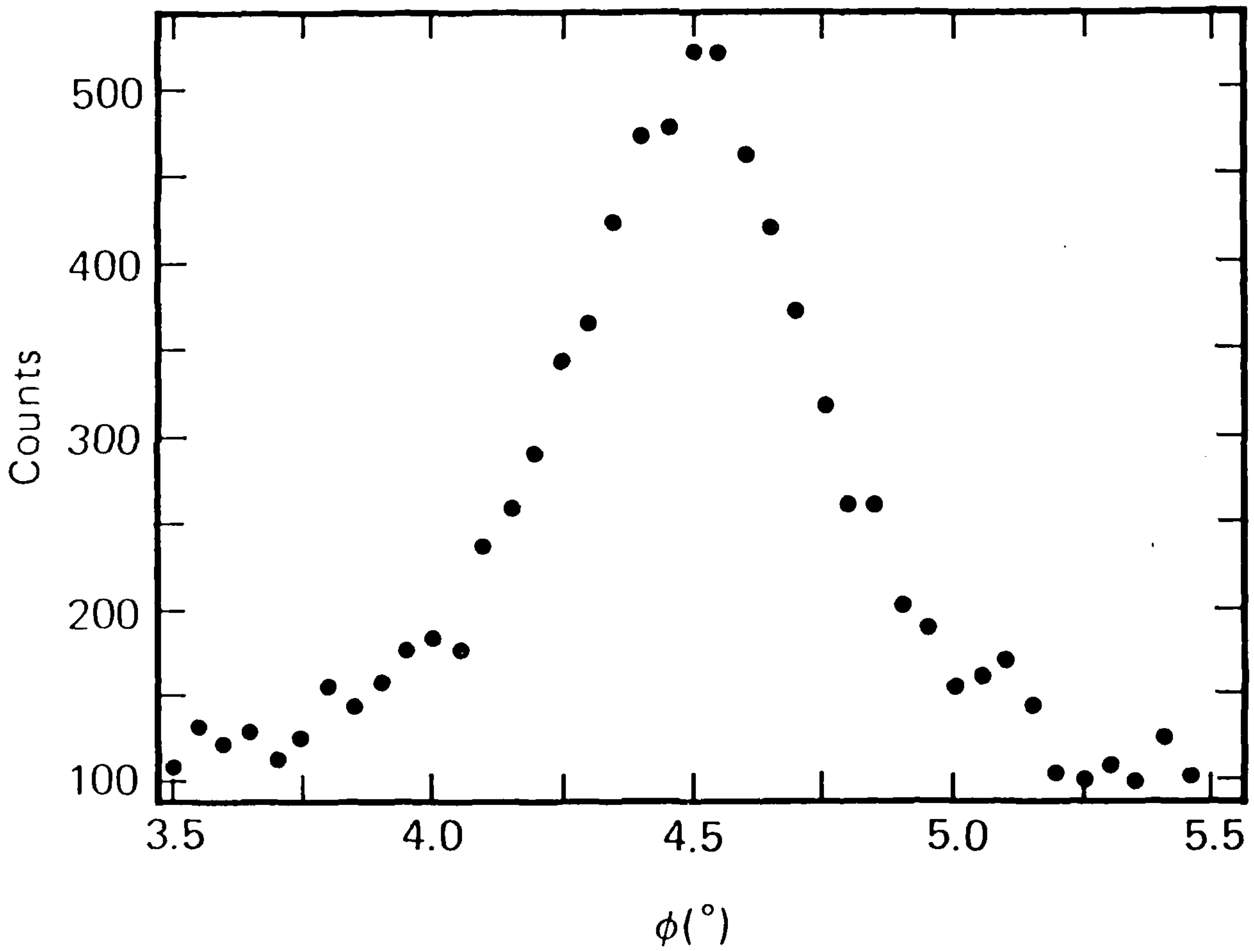

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